

Molecular structure and thermal stability of B_2H_4 and $B_2H_4^+$ species

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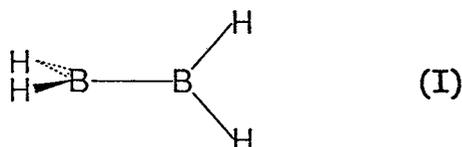
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B_2H_4 has been produced by the reaction of F atoms with B_2H_6 , in successive abstraction reactions. The B_2H_4 species was detected and analyzed by photoionization mass spectrometry. The adiabatic ionization potential of this species (9.70 ± 0.02 eV) and the vertical value (~ 10.4 eV) are obtained from the photoion yield curve. These values, and the shape of this curve, are consistent with a doubly bridged, C_{2v} structure for both the neutral and ionic species. The fragment ion $B_2H_2^+$ is observed, with an appearance potential of $11.53_5 \pm 0.03$ eV. This value, combined with previous results, yields $D_0(B_2H_4-H) \approx 40.1$ kcal/mol, whereas $D_0(B_2H_5-H) \leq 102.7$ kcal/mol. The $B_2H_2^+$ fragment may have as its neutral precursor an isomeric B_2H_4 (D_{2d}), with approximately the same stability as the C_{2v} species. An earlier value for the appearance potential of $B_2H_4^+$ from B_2H_6 is shown to be too high, due to a very small formation probability at the thermochemical threshold.

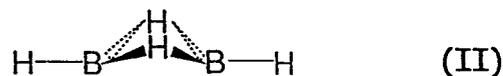
I. INTRODUCTION

Although B_2H_4 has not previously been observed experimentally, it has been the subject of several recent *ab initio* calculations. Vincent and Schaefer¹ studied the D_{2d} structure



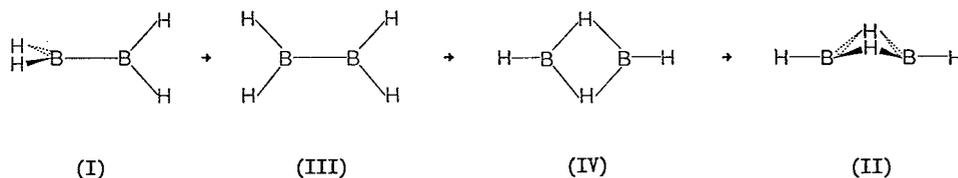
using a double-zeta plus polarization basis set at the single plus double excitation CI level. Mohr and Lipscomb² performed calculations at the MP2/6-31G* level. Both studies concluded that this was the ground state structure, with two perpendicular H-B-H planes, and a barrier to rotation of

about 12 kcal/mol. Mohr and Lipscomb² showed that inclusion of correlation stabilized a nonplanar, doubly hydrogen-bridged C_{2v} structure



so that it was only 1.5 kcal/mol less stable than (I) at the MP2/6-31G* level. Curtiss and Pople³ have reexamined this problem at the G1 level of theory, and concluded that (I) and (II) are essentially equal in energy [with II actually being 0.1 kcal/mol more stable than (I)].

The barrier to isomerization is probably quite high. A possible pathway would be



The transition from (I) to (III), i.e., the barrier to rotation, is the aforementioned 12 kcal/mol. The transition from (II) to (IV) (i.e., the inversion barrier) is given by Curtiss and Pople³ as 26.7 kcal/mol at the HF/6-31G* level. Although correlation effects are not included in this last value, a barrier to isomerization [(I) \rightarrow (II)] of about 30 kcal/mol could be inferred. However, there might be other lower energy pathways.

For the $B_2H_4^+$ cation, the *ab initio* calculations³ predict that a dibridged C_{2v} structure analogous to (II) is clearly

the most stable, with a tribridged C_{3v} structure lying 11.4 kcal/mol higher in energy, and a D_{2d} structure analogous to (I) situated 19.0 kcal/mol above the ground state structure, at the G1 level of theory. These calculations can be summarized in the schematic potential energy diagram of Fig. 1. If, in fact, the C_{2v} and D_{2d} structures of B_2H_4 are essentially equal in energy, the ionization probability for the C_{2v} structure near threshold should be much higher than that of D_{2d} (since the Franck-Condon factors would be much more favorable), whereas the D_{2d} structure would require 19.0

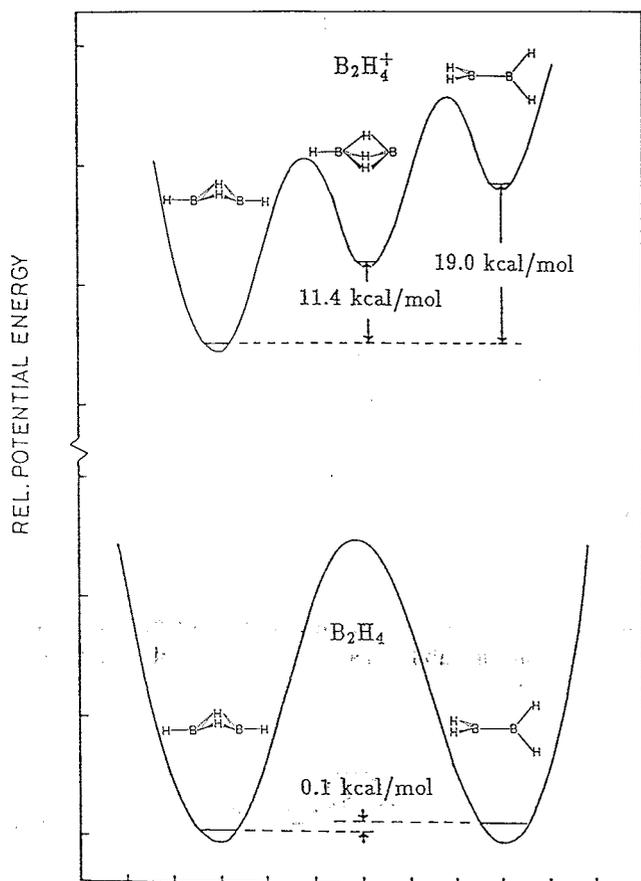


FIG. 1. A schematic potential energy diagram of B₂H₄ and B₂H₄⁺, based on *ab initio* calculations (Ref. 3).

kcal/mol \equiv 0.82 eV to access a favorable portion of the cation potential surface.

Curtiss and Pople³ have also called attention to the fact that their calculated threshold for the dissociative ionization process



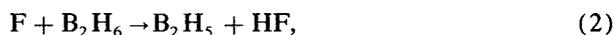
is 11.25 eV, whereas the corresponding appearance potential reported from our laboratory⁴ was \leq 11.75 eV. Their calculations^{5,6} for the appearance energies of B₂H₆⁺, B₂H₅⁺, B₂H₃⁺, and B₂H₂⁺ from B₂H₆ were in better agreement with our photoionization thresholds. Hence, they speculated that the experimental threshold for B₂H₄⁺ corresponded to the formation of the excited C_{3v} configuration, because the formation of the C_{2v} structure of B₂H₄⁺ from B₂H₆ would require removal of two terminal hydrogen atoms from opposite ends of B₂H₆, which could be difficult.

Our goal in the experimental program described below was to prepare B₂H₄ and to obtain its photoion yield curve. The shape of this curve could provide clues about the structure of B₂H₄ which was being detected. Furthermore, the experimental adiabatic and vertical ionization potentials could be compared with the values predicted by *ab initio* calculations, thereby providing another test of the structure and energetics of B₂H₄ and B₂H₄⁺. The thermochemical stability of B₂H₄⁺ (the point of disagreement between experiment and calculation) could be tested by determining the

threshold for a fragment ion from B₂H₄⁺, and by reexamining the threshold for reaction (1).

II. EXPERIMENTAL ARRANGEMENT

The B₂H₄ species was prepared *in situ* by the reaction of F atoms with B₂H₆. This reaction apparently proceeds in two steps,



The B₂H₅ radical is more readily prepared, and is the subject of an accompanying paper.⁷ However, by reducing the B₂H₆ flow rate, it is possible to achieve conditions such that (B₂H₄) > (B₂H₅), as measured by their photoionization yields. The fluorine atoms were generated in a microwave discharge through pure F₂. The fast-flowing fluorine was trapped downstream by a helium cryopump. The description of the flow tube, the reaction cup where F atoms and B₂H₆ interact, and the general photoionization mass spectrometric arrangement has been given previously.⁸ The source of B₂H₆ was a 50% Ar, 50% B₂H₆ mixture obtained from Matheson Gas Products. Initial data were obtained with a wavelength resolution of 0.5 and 0.84 Å (FWHM). Subsequently, a coarser resolution (1.4 Å) was employed to improve the signal-to-noise ratio, particularly near the ionization threshold. This enhanced signal was vital for detecting fragments from the decomposition of B₂H₄⁺. All of the measurements utilized the peak light intensities in the many lined emission spectrum of a discharge in molecular hydrogen.

III. EXPERIMENTAL RESULTS

A. B₂H₄⁺ (B₂H₄)

Preliminary measurements showed that the adiabatic ionization potential of B₂H₄ was considerably higher than that of B₂H₅. However, there was always some B₂H₅ present when conditions were optimized for the production of B₂H₄. These observations afforded us two methods of data presentation, which require some explanation.

The normal isotopic abundance of boron⁹ is ¹¹B = 0.801 and ¹⁰B = 0.199. Thus, B₂H₅⁺ will appear at *m/e* = 27, 26, and 25, with relative intensities of 0.6416, 0.3188, and 0.0396, respectively. These values must be slightly corrected for the variation of transmission function with mass of the quadrupole mass filter. For the moment, we ignore this latter effect, and note that the intensity ratio of *m/e* = 26 to *m/e* = 27 should be 0.3188/0.6416 = 0.4969 when B₂H₅⁺ is detected, but no B₂H₄⁺ is yet detected. When B₂H₄⁺ appears, it will make its contributions at *m/e* = 26, 25, and 24, with the aforementioned abundance ratios. Since B₂H₄ has a higher onset energy than B₂H₅, a plot of the *m/e* = 26 to *m/e* = 27 ratio should be flat and equal to 0.4969 at energies below the ionization potential of B₂H₄, and should begin to increase above this IP. Alternatively, by measuring *m/e* = 27 and *m/e* = 26 at each wavelength, one can correct the *m/e* = 26 intensity for the isotopic contribution of B₂H₅⁺, leaving as a residue the B₂H₄⁺ intensity from the B₂H₄ species. Both of these methods have been utilized in the

treatment of the experimental data.

Figure 2 is a display of these measurements. The $m/e = 27$ to $m/e = 26$ intensity ratio is shown in the threshold region. Also shown is a more extensive, composite data set in which the $B_2H_5^+$ contribution has been subtracted from the $m/e = 26$ intensity. The higher photon resolution has been employed in these experiments. Both curves display a departure from the background level at $\sim 1276 \text{ \AA}$, and also some evidence for step structure. The step structure becomes blurred at shorter wavelengths, and the photoion yield curve ultimately reaches a plateau at $\lambda \lesssim 1160 \text{ \AA}$. The step structure is indicative of a vibrational progression in a direct photoionization transition. The overall band width of this transition is about 0.97 eV. The half-width of this band ($\sim 0.5 \text{ eV}$) and the flat plateau at shorter wavelengths suggests that we are viewing a transition between a single ground state of the neutral species and a single state of the cation. Furthermore, they do not differ greatly in geometry, in contrast to the case of the $B_2H_5 \rightarrow B_2H_5^+$ transition.⁷ A plausible inference, based on the *ab initio* calculations summarized schematically in Fig. 1, is that this experimental photoion yield curve corresponds to a transition between the doubly bridged, C_{2v} structure of B_2H_4 and the corresponding C_{2v} structure of $B_2H_4^+$. The predicted³ adiabatic ionization potential of B_2H_4 is 9.64 eV; our observed onset in Fig. 2 is $\sim 9.72 \text{ eV}$. The difference between the vertical and adiabatic ionization potentials is predicted to be $\sim 0.57 \text{ eV}$;¹⁰ the corresponding value estimated from Fig. 2 is $\sim 0.7 \text{ eV}$.

The normal mode(s) excited in the transition is/are expected to be totally symmetric (a_1). The B-H_t distances in both the neutral and cation are calculated to be nearly identical. The major structural differences occur in the bridge. Both C_{2v} structures are nonplanar (i.e., the bridge is puckered), but the cation has a much lower inversion barrier than the neutral species (3.7 vs 26.7 kcal/mol at the HF/6-31G* level).³ Consequently, the inferred transition is likely to be occurring between two double-well potentials, schematical-

ly drawn in Fig. 3. Hence, one may expect some irregularity in the vibrational increments. Furthermore, the calculated frequencies may not reflect the nuances of a double-well potential.

The observed frequency interval is about $1300 \pm 100 \text{ cm}^{-1}$. The calculated³ frequencies having a_1 character and eigenvectors correlating with a change in bridge structure include 2011 cm^{-1} (H's in bridge separating), 1111 cm^{-1} (B-B stretching), and 877 cm^{-1} (H's in bridge moving up and down). [These frequencies have been scaled by the factor 0.89, often used in comparing calculated (Hartree-Fock) and observed frequencies.] None of these *ab initio* frequencies is in good agreement with the observed interval. The closest is the unscaled B-B stretch (1248 cm^{-1}). This discrepancy may be resolved with a higher level (than HF/6-31G*) calculation, and a more accurate treatment of the double-well potential.

B. $B_2H_2^+(B_2H_4)$

The earlier studies from our laboratory⁴ indicated that the preferred fragment from $B_2H_4^+$ was $B_2H_2^+ (+H_2)$. The other possibilities ($BH_2^+ + BH_2$, $BH^+ + BH_3$, $BH_3^+ + BH$) occur at higher energy and are weaker. In order to enhance the experimental sensitivity for this fragmentation process, which involves cumulative errors, the lower resolution was used. Figure 4 is a photoion yield curve of $B_2H_4^+$ at this lower resolution; also shown in this figure is the ratio of intensities of the $B_2H_2^+$ fragment ion to the $B_2H_4^+$ parent ion. In this latter curve, the $B_2H_2^+$ intensity is an average of the residues at $m/e = 24$ and $m/e = 23$, after contributions from $B_2H_4^+$ and $B_2H_3^+$ have been subtracted. The process of subtraction is sequential— $m/e = 27$ represents only $B_2H_5^+$. Its isotopic contribution to $m/e = 26$ can be calculated and subtracted, leaving as residue at $m/e = 26$ the $^{11}B^{11}BH_4^+$ component. This, in turn, can be used to estimate $^{11}B^{11}BH_3^+$ at $m/e = 25$. The $B_2H_3^+$ from B_2H_5 turns out to

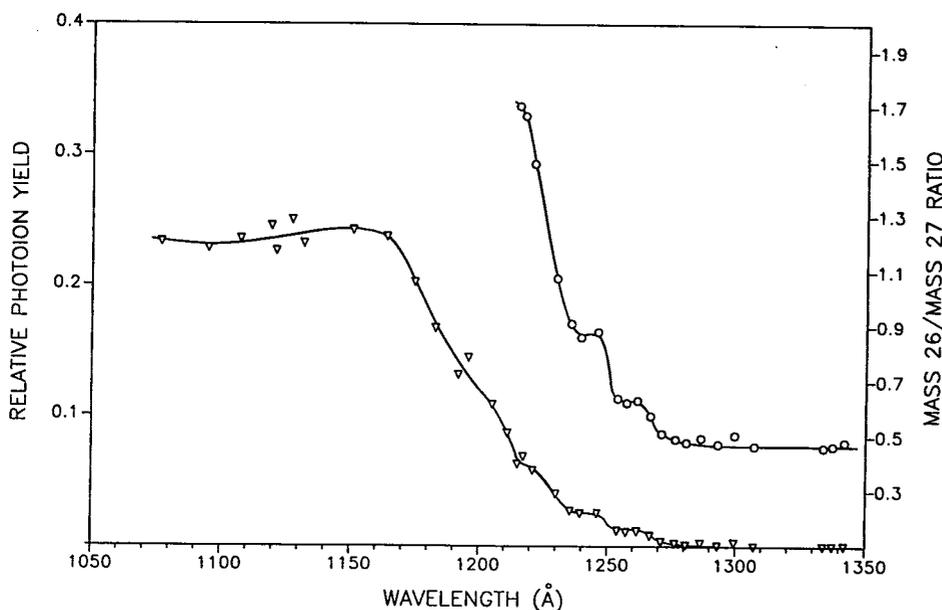


FIG. 2. The photoion yield curve of $B_2H_4^+$ (B_2H_4), obtained with a wavelength resolution of 0.5 \AA (∇). Also shown is the $m/e = 26$ to $m/e = 27$ intensity ratio (\circ), which should mimic the photoion yield curve (see the text).

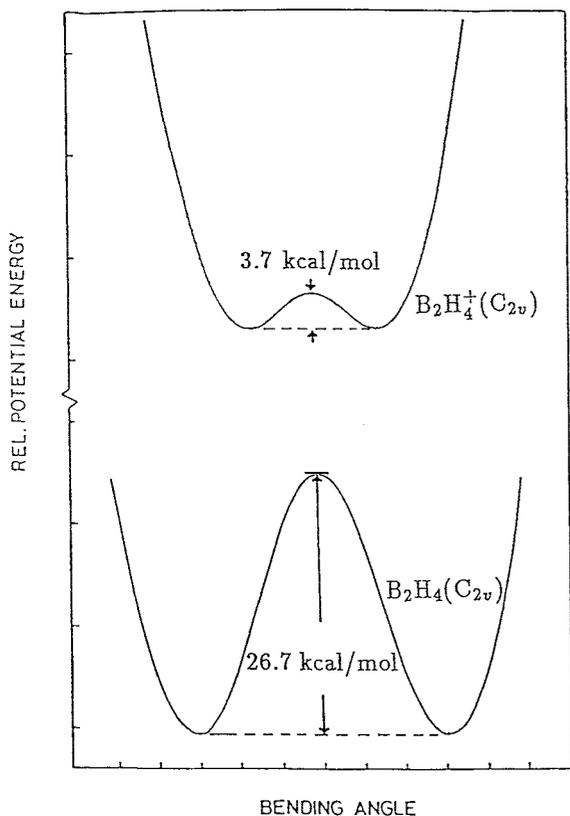
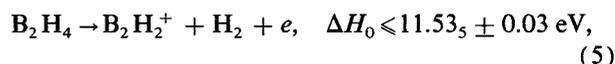
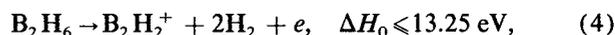


FIG. 3. A schematic potential energy diagram of the C_{2v} , double hydrogen bridged structures of B_2H_4 and $B_2H_4^+$.

be the largest undesired contributor to $m/e = 24$, and is of approximately the same magnitude as $^{11}B^{11}BH_2^+$. The resulting curve representing $(B_2H_2^+)/ (B_2H_4^+)$ has significant scatter, and a sloping base line. The origin of the sloping background is not apparent. Several possible causes were examined, including variation of the isotopic abundance, the

mass dependence of the transmission function, and "leakage" from insufficient mass resolution. Within allowable experimental variation, none of these factors could account for the sloping base line. The extrapolated, sloping "background" cannot be characteristic of a $B_2H_2^+$ onset, with any reasonable choice of thermochemical bond energies. The first clear departure from the sloping background level occurs at $\sim 1076 \text{ \AA} \equiv 11.523 \text{ eV}$. An extrapolation to the sloping background line yields $\sim 1082 \text{ \AA} \equiv 11.459 \text{ eV}$. The average of these values, $11.49 \pm 0.03 \text{ eV}$, would appear to be a conservative choice. When corrected for the internal thermal energy of B_2H_4 at 300 K (using the internal heat content of C_2H_4 , 0.045 eV, as an estimate), the 0 K appearance potential of $B_2H_2^+$ from B_2H_4 becomes $\leq 11.53_5 \pm 0.03 \text{ eV}$.

The onset energy of $B_2H_4^+$, as depicted in the lower resolution but higher sensitivity curve of Fig. 4, is $\sim 1280 \text{ \AA} \equiv 9.686 \text{ eV}$. With the available data, it is difficult to deduce the rotationally adiabatic value, and hence we choose the mean of the onset energies obtained from Figs. 2 and 4, i.e., $9.70 \pm 0.02 \text{ eV}$, as the adiabatic ionization potential of B_2H_4 . From the peak of the energy derivative of this curve, we obtain 10.42 eV for the vertical ionization potential. By combining the thresholds for $B_2H_2^+$ from two processes, one previously determined⁴ from B_2H_6 and the presently obtained value from B_2H_4 , i.e.,



we deduce $\sim 1.71_5 \pm 0.03 \text{ eV} \equiv 39.5 \pm 0.7 \text{ kcal/mol}$ for the reaction



Curtiss and Pople^{3,6} have obtained 37.2 (± 2) kcal/mol for this process, at the G1 level of theory. Both of the experimental thresholds entering into this computation are rigorously only upper limits. Of the two, the threshold from B_2H_6 is

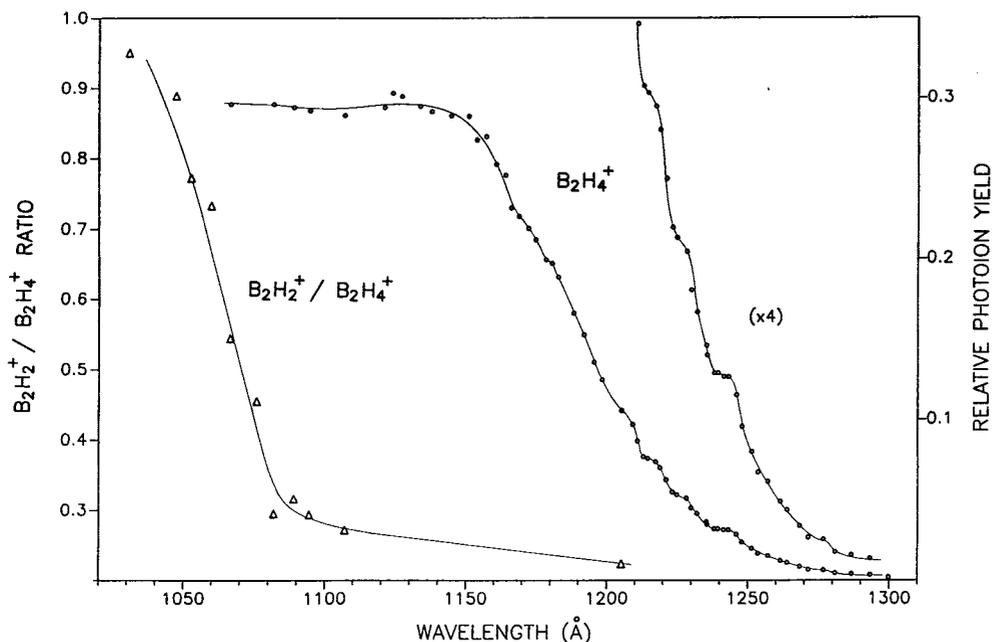


FIG. 4. The photoion yield curve of $B_2H_4^+(B_2H_4)$ and the ratio $(B_2H_2^+)/ (B_2H_4^+)$, the latter obtained with a wavelength resolution of 1.4 Å (FWHM).

more likely to be too high, since it represents the second stage of successive decompositions ($B_2H_6^+ \rightarrow B_2H_4^+ \rightarrow B_2H_2^+$). A slightly lower value for this threshold would improve the agreement between experiment and theory. In fact, if we introduce the enthalpy 13.15 eV for reaction (4), as calculated by Curtiss and Pople, the endothermicity of reaction (6) becomes 37.2 kcal/mol, which is fortuitously the precise value given by the calculations.

If $D_0(H_2) = 103.268$ kcal/mol is combined with the enthalpy of reaction (6), one infers 142.8 kcal/mol as the energy required to remove two hydrogen atoms from B_2H_6 . From our study of B_2H_5 ,⁷ we deduced that ≤ 102.7 kcal/mol was required to remove the first hydrogen atom, and hence, the bond energy (0 K) for the process



requires only ~ 40.1 kcal/mol. Curtiss and Pople¹¹ obtain 100.0 kcal/mol for the first bond energy, and 40.6 kcal/mol for the second.

We now turn our attention to the discrepancy between calculated and observed thresholds for reaction (1), discussed in Sec. I. An alternate path for deducing the endothermicity of reaction (1) is to add the experimental enthalpy of reaction (6) to the experimental adiabatic ionization potential of B_2H_4 . The resulting quantity, 11.415 ± 0.04 eV, is closer to the calculated value (11.25 eV) than to the previously reported appearance potential (≤ 11.75 eV). Furthermore, the experimentally derived energy for reaction (6) may be slightly higher (as discussed earlier). If this is the case, the present experimental result corresponding to reaction (1) would be even closer to the calculated value, and within the anticipated margin of error in the *ab initio* calculations (± 0.1 eV). This prompted us to reexamine the directly determined threshold for reaction (1) from B_2H_6 . In Fig. 5, we display the new measurements of the photoion yield curves of $B_2H_5^+$ and $B_2H_4^+$ from B_2H_6 , and also the ratio of intensities of $B_2H_4^+/B_2H_5^+$ as a function of wavelength. It is evident from these figures that $B_2H_4^+$ plunges more rapidly to an apparent threshold, but then displays pronounced curvature as it approaches the background level, whereas $B_2H_5^+$ has a more gradual approach to the base line. Previously,⁴ we described our choice for the $B_2H_5^+$ threshold as a subjective judgment of the departure from the background level, whereas the threshold for $B_2H_4^+$ was determined by extrapolation of the linear portion of its photoion yield curve. This tended to exacerbate the difference in these two thresholds. In hindsight, it appears that both fragments exhibit a gradual onset, but the $B_2H_4^+$ photoion yield has a much more pronounced curvature. It would be very difficult to determine the "true" onset from such a curve. These experimental results imply that there is a very low probability of forming the doubly bridged, C_{2v} structure of $B_2H_4^+$ from B_2H_6 at the adiabatic threshold, which is essentially the surmise of Curtiss and Pople.³

IV. DISCUSSION AND CONCLUSIONS

A B_2H_4 species has been produced by the successive hydrogen abstraction reactions of F atoms with B_2H_6 . The

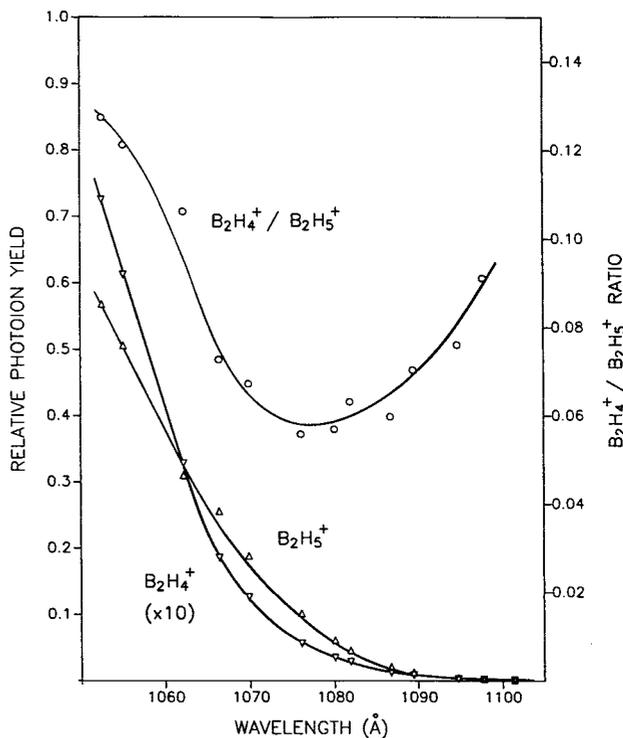


FIG. 5. The threshold regions of the photoion yield curves of $B_2H_5^+$ (B_2H_6) and $B_2H_4^+$ (B_2H_6). Also shown is the ratio of intensities $B_2H_4^+ : B_2H_5^+$ as a function of wavelength.

photoion yield curve of this species yields an adiabatic ionization potential of 9.70 ± 0.02 eV, a vertical ionization potential of ~ 10.4 eV, and some step structure indicative of a vibrational progression, with $\omega \approx 1300 \pm 100$ cm^{-1} . These results are in essential agreement with *ab initio* calculations, if the B_2H_4 species detected has a doubly bridged, C_{2v} structure. However, these calculations also predict an isomeric B_2H_4 species (D_{2d} , with a B-B bond) which has almost exactly the same stability, and which should have an adiabatic ionization potential of ~ 10.5 eV. Although there is no marked increase in the $B_2H_4^+$ photoion yield curve at this photon energy (~ 1180 Å), it is possible that the $B_2H_2^+$ fragment results from ionization of the D_{2d} isomer of B_2H_4 . Curtiss¹⁰ has calculated a gap of ~ 4.4 eV between the first and second vertical ionization potentials of the C_{2v} isomer. Since the vertical IP of the ground state is ~ 10.4 eV, the first excited state should occur at ~ 14.8 eV $\equiv 838$ Å. The $B_2H_2^+$ threshold occurs well below that value (~ 1080 Å $\equiv 11.48$ eV), and this fragment ion attains an intensity approximately equal to that of the parent ion at ~ 1030 Å $\equiv 12.0$ eV. Thus, the fragment ion would appear to be formed in the Franck-Condon gap between these two states, and nonetheless, acquires an intensity comparable to that of the parent ion, which derives its intensity from a strong ionization process. The calculations of Curtiss¹⁰ do not yet include correlation effects, but a substantial reduction in the gap between the two states would be required to alter this deduction. The proportionately large intensity of $B_2H_2^+$ within ~ 0.5 eV of its threshold is suggestive of a relatively large ionization probability at 12 eV, characteristic of the presence of a new

state, rather than a transition in the Franck–Condon gap. For comparison purposes, the fragment ion $C_2H_2^+$ from C_2H_4 appears within the latter half of an excited state, but is only about half the intensity of $C_2H_4^+$, 1.5 eV beyond the fragmentation threshold.¹²

For the D_{2d} isomer of B_2H_4 , Curtiss¹⁰ has calculated vertical ionization potentials of 11.8 and 13.3 eV, at the Hartree–Fock Koopmans' theorem level. At a much higher (G1) level of calculation Curtiss and Pople³ have computed that the adiabatic first ionization potential of the D_{2d} isomer is 10.46 eV. Hence, it is quite plausible that the onset and growth of $B_2H_2^+$ (B_2H_4) in the 11.48–12.0 eV region occurs by initial ionization of the D_{2d} species of B_2H_4 , and its subsequent decomposition. If this interpretation is correct, then the relative intensities of $B_2H_2^+$ and $B_2H_4^+$ at ~ 12.0 eV ($\sim 1:1$) would be crude measures of the relative abundance of the D_{2d} and C_{2v} forms of B_2H_4 . If the recent *ab initio* calculations are correct, and if the dynamic equilibrium between these species is attained in the reaction chamber, these isomers should have approximately equal abundance. The D_{2d} species should also contribute to the higher energy portion of the $B_2H_4^+$ photoion yield curve, but it may be more difficult to observe this contribution, if it gradually adds to the already substantial $B_2H_4^+$ intensity from ionization of the C_{2v} structure.

In conclusion, the fragment species $B_2H_2^+$ from B_2H_4 has an appearance potential (0 K) of $11.53_5 \pm 0.03$ eV. From this value, and earlier work, one can infer $D_0(B_2H_5-H) \lesssim 102.7$ kcal/mol and $D_0(B_2H_4-H) \simeq 40.1$ kcal/mol, both values in rather good agreement with recent *ab initio* calculations.

A discrepancy between earlier experimental results for the appearance potential of $B_2H_4^+$ from B_2H_6 and corre-

sponding *ab initio* calculations has been clarified. The probability of forming $B_2H_4^+$ from B_2H_6 at the thermochemical threshold is extremely weak, and therefore the usual treatment of fragment onsets is not applicable.

From the enthalpy of reaction (6), we can deduce that $\Delta H^\circ_{f0}(B_2H_4) \leq 52.0 \pm 0.7$ kcal/mol. The isolated molecule is stable to decomposition into two BH_2 radicals by ~ 108 kcal/mol, and into $BH + BH_3$ by ~ 80 kcal/mol. It is, of course, unstable with respect to solid boron and H_2 by 52 kcal/mol, and it can react with excess B_2H_6 to form B_4B_{10} , liberating about 45 kcal/mol.

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